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A Thesis
Submitted to the Department of Metallurgy
in Partial Fulfilment of
the Requirements for the Degree of
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ABSTRACT

A series of boron steel alloys were made. The composition of which are: .01 per cent boron, .02 per cent boron, .03 per cent boron, .04 per cent boron and .05 per cent boron.

The maximum effect on depth of hardening and hardness was obtained with the addition of .03 per cent boron.

INTRODUCTION

Many attempts have been made to improve iron and steel and their alloys by the addition of boron. The results obtained were not encouraging for the reason that the amount of boron used, generally from 0.2 to 2.0 per cent is altogether too high. This percentage of boron renders the product hard and brittle and of late the experiments with boron in this connection have been practically abandoned.

It appears that Walter was perhaps the first to appreciate the fact that extremely small percentages of boron were effective in improving some of the properties of steel. Also, the amounts previously used were far in excess of those necessary and resulted in making the steel brittle and hot short. He did not appreciate the effect of boron on the hardenability of steel, and it is this effect with which this thesis is most concerned.

THEORETICAL CONSIDERATIONS OF HARDENABILITY

The maximum hardness that can be obtained in a heat treatable plain carbon or low alloy steel is dependent almost entirely on its carbon content. Alloying elements have a minor effect, but in an alloy steel containing less than 5 per cent of alloys, the effect on the maximum obtainable hardness is not significant. Alloys would thus seem to be of little value in increasing the surface hardness of heat treatable steels as the maximum hardness that can be obtained is practically independent of the alloy content. The maximum hardness is determined almost entirely by the carbon content and the rate of cooling. The rate of cooling necessary to harden a plain carbon steel is, however, such that this rate is reached for only a relatively small distance in from the quenched surface and so this steel is hardened for only this distance. When the section is quite small and the quench is drastic, the steel may be hardened substantially throughout. However, when the section is relatively large, the interior which cooled at a rate lower than that required to obtain full hardness is left comparatively soft. Such a steel is a shallow hardening steel.

Broadly speaking, the strength of any steel varies directly as its hardness. Therefore, a shallow hardening steel would, in large sections, have only a comparatively narrow high strength zone on the outside and a relatively large low strength zone in the interior. The average

strength would thus be low as compared to a steel having a wider or deeper zone of high hardness and strength.

Alloys, by lowering the rate of cooling necessary to harden a steel, widen the zone that cools rapidly enough to harden. As a result, sections which would be hardened for only a short distance from the surface if made of plain carbon steel, and be correspondingly weak, are hardened and strengthened throughout. Because of this the piece as a whole is correspondingly stronger if made of an alloy steel. The depth to which a steel will harden, either fully or to some specified hardness, when quenched is a measure of its hardenability.

High carbon content tends to lower the critical cooling rate, thereby increasing the hardenability. The effect of carbon content on critical cooling rate has been determined by several investigators. The results obtained by Digges (1)* may be summarized as follows:

"With constant austenitic grain size and complete solution of the carbon in the austenite, the critical cooling rate decreased continuously with increase in the carbon content of the alloys. The hypereutectoid alloys thus had slower critical cooling rates (greater) hardenability), than either the alloys of eutectoid or

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(1)* - Refer to bibliography

hypoeutectoid composition. However, a small change in the carbon content of the lower carbon alloys had a more marked effect on the critical cooling rate than did a corresponding change in the higher carbon alloys.

"The carbon content of the austenite, therefore, had a pronounced influence on the hardenability of the alloys. Full depth of hardening is obtained in these alloys only when all the carbon is in solution in the austenite.

"Under similar conditions with respect to austenitic grain size, carbon content, and complete solution of the carbon in the austenite, the high purity iron-carbon alloy hardened less deeply than do plain carbon steels."

According to Heyer (2)* other elements effect the hardenability. The different elements and their effect may be summarized as follows:

"It has been found that certain carbide forming elements such as vanadium and molybdenum tend to stabilize the carbides present and reduce their tendency to dissolve in the austenite at ordinary heat treating temperatures. Likewise certain elements such as aluminum and vanadium may be present as very finely divided oxides which are even less soluble in austenite. In either case such alloying elements may reduce the

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(2)* - Refer to bibliography

hardenability by introducing transformation nuclei, even though it has been shown that they tend to increase hardenability provided they are fully dissolved in the austenite at the quenching temperature. These particles probably tend to obstruct grain growth of the austenite, thus fine grain size may contribute further to reduced hardenability.

"In the case of aluminum the normal tendency is definitely towards fine grain size "abnormal" McQuaid-Ehn microstructures, and reduced hardenability, regardless of the basic cause of these related results. A theory quite different from the fine grain size-nucleation theory is offered by Morris and McQuaid who attribute the low hardenability of certain carbon steels to the presence of low carbon austenitic areas at the quenching temperature, resulting in separation in primary ferrite and a very high transformation rate in the 1000° F. region, thus preventing the formation of a fully martensitic structure even at the highest commercial cooling rates. On this premise the effect of alloying elements is explained as follows:

" ' Theoretically all that is necessary to prevent ferrite formation in the boundaries on quenching is to increase the temperature or time to the point where carbon diffusion across the boundaries had taken place and then to cool at a fast enough rate to retain the

carbon in solution.

" ' Any element or combination of elements in the boundaries that will decrease the carbon solution will aid in the austenite transformation and decrease hardenability. Conversely, any element which aids in the carbon solution or stabilizes the austenite formed will increase the hardenability.

" ' We have seen that the pure iron-carbon combinations are inherently shallow hardening and the addition of many metallic elements will increase the hardenability. Even aluminum in sufficient quantity decreases the critical cooling rate and hence increases the hardenability. This is only true, however, when the temperature is sufficiently high and the time sufficiently long to insure complete carbon solution and uniform diffusion.' "

REVIEW OF ASSOCIATED RESEARCH

During recent years some research has been carried on to determine the effect of small additions of boron to cast iron. Guillet[3]* studied a series of nine cast irons which were made in a small electric furnace. Boron was introduced by a ten per cent ferroboron. Much boron was lost when melting in the arc type furnace under a slag deoxidized with ground wood charcoal. Recoveries were better in a small high frequency furnace using a slag of molten silica and glass. Boron in the alloys ranged from zero to one per cent; other elements were reasonably constant and about: total carbon 3.5 per cent, silicon 1.5 per cent, manganese 0.45 per cent, sulphur 0.01 per cent, and phosphorous 0.05 per cent.

In the first series of castings so made that the boron-free iron had a chill 1/8 inch deep, boron had a little effect until it exceeded 0.1 per cent. However, a composition of 0.2 per cent boron produced a one inch chill. It was found that when the boron content reached 0.4 per cent the test casting was entirely white. Microscopic examination of these samples showed no unusual features.

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(3)* - Refer to bibliography

Boron does have an observable effect on the free graphite. The amount determined chemically as graphitic carbon steadily decreases with increasing boron and under the microscope the number of particles and the length and thickness of the filament decreases. Again, when the percentage of boron increases, the graphite filaments tend to accumulate in colonies. This distribution being particularly marked in the cast iron containing 0.18 per cent of boron, which has reduced the graphitic carbon from an original 2.7 to 1.25 per cent.

Graphitization of these white irons was studied, and some interesting data secured concerning the "A_o anomaly" of cementite at about 400° F. Increasing amounts of boron raised this temperature; at 0.3 per cent boron it is 450 F., at 0.65 per cent boron it is 500 to 575 F., and at one per cent boron it is 575 to 625 F. The rate of graphitization may be inferred by the changes in the amplitude of the A_o range during repeated heatings and coolings. If the boron is less than 0.2 per cent, these changes are what would normally be expected in a boron-free iron. With higher boron, the A_o changes are stabilized after the first heating cycle. This stabilization

indicates a constant amount of cementite- that is to say, higher boron has a marked restraint on the decomposition of cementite.

Hardness changes after the annealing cycles agreed with these conclusions. Graphitization of the 0.3 per cent boron was practically finished with one cycle, the hardness having dropped from 635 to 205 Brinell. After four cycles the 0.65 per cent boron iron dropped from 636 to 284 Brinell. In the case of the iron with one per cent boron it softened only to 436 Brinell, with practically no action on further reheatings after the second. In the range of boron contents studied by the investigator, this element does not appear to effect the temperature at which growth accompanied by graphitization occurs.

Hardness induced by the boron was studied in the first series of castings described at the beginning. Brinell hardness of the chill increased directly with the boron content from 520 for the boron-free iron to 626 for the 0.4 per cent boron iron. Center hardness also increased proportionately, 190 for the gray iron, boron free, up to 502 for the all white iron containing 0.4 per cent boron.

Shear strength increased from about 30,000 psi. for boron free to 45,000 psi. for 0.2 per cent boron. The static transverse strength increased from 140,000 to 200,000 for the same limits. Young's Modulus increased from 12,000,000 to 22,000,000 psi. Deflection at rupture held rather constant to 0.1 per cent boron, but then dropped sharply.

Chemical analysis is difficult and the method finally adopted was suggested by the Creusolt laboratory. The sample was dissolved in dilute H_2SO_4, the solution neutralized and a mixture of alcohol and glycerine added. This forms a glycero-boric complex which is titrated with 0.1 N caustic soda with a phthalein indicator. The caustic soda is standardized against a solution of borax treated in the same way.

(3)*

The conclusions emerging from these tests on boron cast irons may be briefly summarized:

"1. As had previously been indicated, boron inhibits the graphitization of cast iron when they are solidifying, and acts as an energetic whitener of the structure.

"2. Boron similarly opposes graphitization

during annealing, by slowing down the speed of decomposition of the cementite, but it does not appear to affect the temperature of incipient graphitization, at least in the range of boron contents studied by the investigators.

"3. Boron uniformly and rapidly raises the A_o temperature.

"4. A small amount of boron raises the mechanical properties (hardness, transverse and shear strength) of gray cast irons, but reduces their capacity for deformation (deflection)."

Whitney (4)* made investigations on low-carbon steels to which he added varying amounts of high-metallic boride crystals. Boron and borides have long been recognized for their ability to influence the physical properties of base metals. This high-metallic boride crystal is applicable to all the many known uses of boron and borides. Also, it has a wide range of additional applications.

For example, a 10 per cent mixture of the crystals, when introduced into a melt of low-carbon steel, will produce a very dense grained alloy which has a hardness of 682 Brinell as it is cast. This alloy may be annealed to machinable softness.

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(4)* - Refer to bibliography

Furthermore, it is claimed that such an alloy possesses an inherent strength and resistance to both abrasion and corrosion far beyond that of hardened steel.

EXPERIMENTAL WORK

Since boron differs from other alloying elements in that extremely small percentages are used; a diluted form of boron is desirable. The boron alloy used in this work has the trade name "Borosil" and is manufactured by the Ohio Ferro-Alloys Corporation. This alloy is formulated to give a uniform dissemination of boron throughout the steel.

This element does not occur in nature in the free state, but is found combined with hydrogen and oxygen, forming boric or boracic acid, $B(OH)_3$, and its salts. Of these the latter is the most important.

"Boron is the only common element, solid under ordinary conditions, whose structure is not known and whose properties are not well understood." (5)* This is surprising when one considers that compounds of boron have been easily available and have been exploited for a very long time. The use of borax as a metallurgical flux goes back to antiquity, and boric acid was isolated from borax by Homberg in 1702.(5)* In 1807 Davy(5)* reported the electrolytic decomposition of boric acid. In the following year

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(5)* - Refer to bibliography

(5)*
Gay-Lussac and Thenard obtained boron as black powder by the reduction of boric acid by potassium. They identified their new product as a new element, to be placed beside carbon.

The properties reported for boron are not accurate because the purity of the samples is doubtful. The properties that have been found for the massive material are reported here. The black solid has a metallic luster, and both vitreous and polymicrocrystalline forms have been described. Conchoidal fracture is frequently noticed. Its density is 2.33. There is a general agreement in the literature that boron is softer than diamond but harder than the sapphire. Mellor and his co-workers were able to scratch carborundum with boron. The melting point is probably near 2200° C. The electrical conductivity of boron is not known with certainty, but it increases with an increase in temperature.

The chemical behavior of massive boron has not been studied extensively. It is inert toward water and toward hydrochloric and hydroflouric acids of all concentrations at their boiling points. It is rapidly attacked by bromine and chlorine above 400° C.

The first problem was to determine the boron content in the "Borosil". The procedure for the boron determination is as follows.

A one gram sample of pure calcium oxide is ignited to constant weight over a blast lamp and then transferred to a dry Erlenmeyer receiving flask. The crucible in which the lime was heated and weighed is set aside in a desiccator for later use.

Crystalline boron is scarcely attacked by acids or alkaline solutions; the amorphous form, however, is soluble in concentrated nitric and sulphuric acids. Both forms fused with potassium hydroxide are converted to a potassium metaborate.

0.1 grams of the alloy was then fused with potassium hydroxide, and neutralized with dilute hydrochloric acid. The solution is then made slightly alkaline by the addition of a few drops of dilute sodium hydroxide solution. The solution is then made slightly acid again by adding a small amount of acetic acid.

The slightly acid solution was then transferred to a pipette-shaped retort, by means of an attached funnel, washing out the beaker and funnel with three 2 to 3 cc. portions of water. The stopcock of the

funnel is closed and connected to the condenser. The paraffine bath, which is never heated over 140° C. is placed in position and the liquid in the retort distilled into the receiver containing the known amount of lime. When all the liquid has distilled over, the paraffine bath is lowered, the retort is allowed to cool for a few minutes, 10 cc. of ethyl alcohol added to the residue in the flask and the contents again distilled by replacing the paraffin bath. The contents of the flask, which are now alkaline are made distinctly acid by the addition of acetic acid, and three more distillations made with 50 cc. portions of ethyl alcohol as before. The paraffine bath is now removed, the receiving flask is stoppered, the contents thoroughly mixed by shaking, and set aside for an hour or more for complete saponification of the ethyl borate. The contents are now poured into a large evaporating dish and evaporated on a water bath at a temperature below the boiling point of the alcohol. Loss of boric acid will occur if the alcohol boils. The adhering lime in the receiving flask is dissolved by wetting its entire surface with a few drops of dilute nitric acid (the flask being inclined and revolved to flow

the acid over its sides). The contents are then transferred to the dish with a little water and the evaporation repeated. No loss of boric acid will take place at this stage, the alcohol having been removed during the first operation. The residue is then gently heated to remove any calcium acetate that may have formed. The cooled borate and lime are taken up with a little water and transferred to the crucible in which the lime was heated and weighed. The contents of the crucible are then evaporated to dryness on the water bath, then heated very gently over a flame (the crucible being covered) and finally more strongly. The heating is continued until a constant weight is obtained. The increase in the weight of the lime represents the amount of B_2O_3 in the sample. The average of several determinations showed the alloy to contain 3.39 per cent boron.

The steel used for the alloys contained 0.12 % carbon.

The alloys were prepared in a coreless induction furnace. This furnace is manufactured by the Ajax Electrothermic Corporation. It has a 1/8 pound capacity, and uses 3 kilowatts at 50,000 cycles. The maximum temperature attainable is 2500° C.

For boron to be effective it is essential that it be added to the steel in such a way that it be substantially protected from oxidization or other chemical combination. It is also necessary that it be uniformly distributed throughout the molten metal. The commercial compound that was used for this express purpose was "Simanal". This compound is manufactured by the Ohio Ferro-Alloys Corporation, and has the following composition- 20 per cent Si, 20 per cent Mn, 20 per cent Al and the balance Fe. To each alloy 1/4 of a gram of "Simanal", as a solid, was added to each alloy. The weight of each alloy as compared to the deoxidized was: 25 grams of alloy to 1/4 gram of "Simanal".

The theoretical amounts of steel and "Borosil", needed to make boron alloys of 0.01 per cent, 0.02 per cent, 0.03 per cent, 0.04 per cent and 0.05 per cent were weighed out and placed in the furnace crucible.

Also, the predetermined amount of "Simanal" was added to each alloy. The alloys were analyzed for boron.

After some preliminary tests the Gooch method of analyzing for boron was found to be some what unsatisfactory when working with material containing such small amounts of boron. I found that the titration of the boric acid in the presence of glycerol was a very accurate method for analyzing alloys containing small amounts of boron.

This method takes advantage of the fact that boric acid reacts neutral to methyl orange, but is acid to phenolphthalein, and may be quantitatively titrated in the presence of glycerol, which prevents the hydrolization of sodium borate. If insufficient glycerol is present the color change takes place too soon, the color fading upon adding more of these substances. The end point is reached when the further addition of these reagents produces no fading of the color. In the procedure, the alkali is neutralized in the presence of methyl orange, and the liberated boric acid is now titrated.

A 0.1 gram sample of the alloy was weighed out. It was then dissolved in cold aqua regia, the insoluble

filtered off and the filtrate brought up to 100 cc. Methyl orange indicator is added and the solution is titrated with 0.1 normal sulphuric acid until the yellow color is replaced by an orange red. From this titration the combined alkali together with any free alkali is calculated, if free alkali is known to be absent the amount of borax may be calculated.

One cc. N. H_2SO_4--0.1911 gram $Na_2B_4O_7$ 10 H_2O or 0.101 gram $Na_2B_4O_7$.

The liberated boric acid may now be titrated with caustic. This may be accomplished either on the above portion or on a fresh 100 cc. portion (free from methyl orange indicator), to which the amount of acid required to neutralize the alkali has been added. Fifty cc. of neutral glycerol is added, followed by phenophthalein indicator. Normal 1/10 sodium hydroxide is added from a burette until a change of color takes place. Methyl orange indicator first becomes yellow, and changes gradually to an orange red. In the absence of methyl orange the characteristic lavender or purplish pink of alkali phenolphthalein is obtained. More glycerol is now added and if the color fades the titration is continued until the addition of these reagents no longer produces a fading of the end point, from this titration the boric

acid content is calculated and the equivalent amount of boron.

Following are the results of the analysis as compared to the theoretical amounts;

Alloy #1 (.01 per cent B) ..... 0.009 per cent B

Alloy #2 (.02 per cent B) ..... 0.018 per cent B

Alloy #3 (.03 per cent B) ..... 0.025 per cent B

Alloy #4 (.04 per cent B) ..... 0.036 per cent B

Alloy #5 (.05 per cent B) ..... 0.042 per cent B

The major portion of each alloy is iron. The other components of the alloy are Mn, Si, Al and C.

From each alloy a small section was cut, and prepared for hardness measurements. For each section, the maximum hardness as cast was determined.

In order to determine the depth of hardness, the speciman being tested was heated to approximately 900° C. and quenched in water.

The Rockwell Superficial Hardness Tester was used to obtain the hardness readings. The diamond point was used as the penetrater with a 30 kg. load. The size of the speciman used in this series of tests is rather small, measuring 2 cm. in length, 2 cm. wide and 1½ cm. in thickness.

According to Burns(7)*, "to describe the hardenability of a steel, two factors should be measured: (1) the maximum attainable hardness, and (2) the 'penetration' effect."

(7)* - Refer to bibliography

REPORT OF RESULTS

Below is listed the maximum hardness of each alloy:

Alloy #1 (.01 per cent B)..... 30-N-49

Alloy #2 (.02 per cent B)..... 30-N-51

Alloy #3 (.03 per cent B)..... 30-N-75

Alloy #4 (.04 per cent B)..... 30-N-70

Alloy #5 (.05 per cent B)..... 30-N-56

The original steel had a hardness of 30-N-39 after given the same treatment as the alloys.

The above results are shown graphically in Fig. 1.

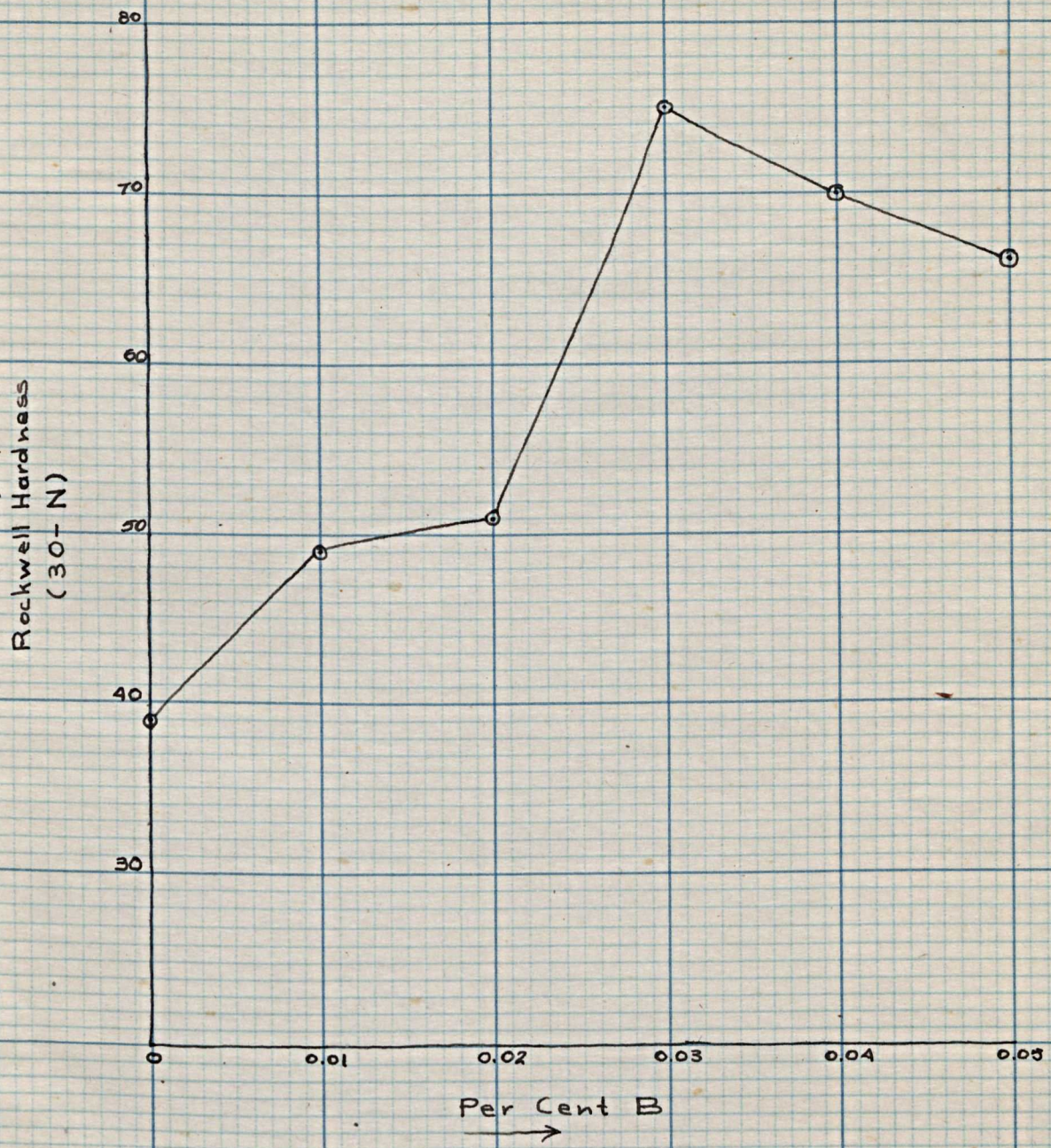

80
70
60
50
40
30
Rockwell Hardness
(30-N)
0
0.01
0.02
0.03
0.04
0.05
Per Cent B

Fig. 1

Below are listed the hardness readings taken through a center section of the speciman.

Alloy #1

(.01 % B)

Distance From The Upper Face	Hardness 30-N
0 cm.	49
½ cm.	49
1 cm.	48.5
1½ cm.	49
2 cm.	49

The above data is represented graphically in Fig. 2.

Alloy #2

(0.02 % B)

Distance From The Upper Face	Hardness 30-N
0 cm.	51
½ cm.	51
1 cm.	50
1½ cm.	50.5
2 cm.	51

See Fig. 3.

Alloy #3

(0.03 % B)

Distance From The Upper Face	Hardness 30-N
0 cm.	76
½ cm.	76
1 cm.	75.5
1½ cm.	76
2 cm.	76

See Fig. 4.

Alloy #4

(0.04 % B)

Distance From The Upper Face	Hardness 30-N
0 cm.	70
½ cm.	69.5
1 cm.	69
1½ cm.	69.5
2 cm.	70

See Fig. 5.

Alloy #5

(0.05 % B)

Distance From The Upper Face	Hardness 30-N
0 cm.	57
½ cm.	55.5
1 cm.	55
1½ cm.	56
2 cm.	57

See Fig. 6.

Fig. 2

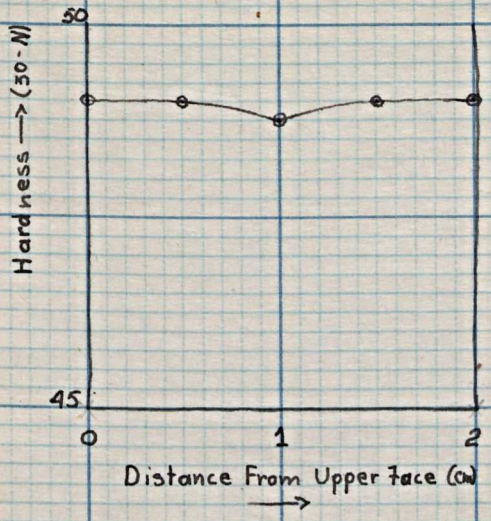


Fig. 3

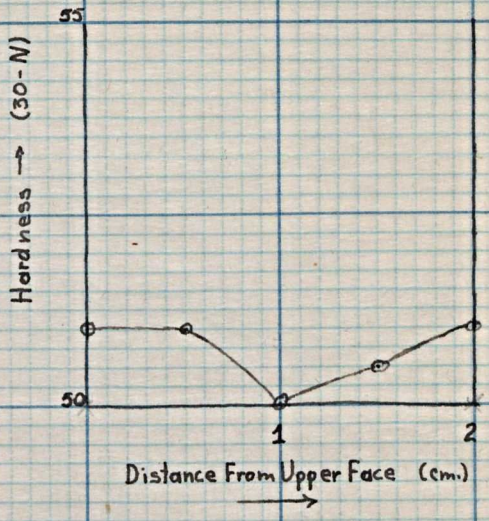


Fig. 4

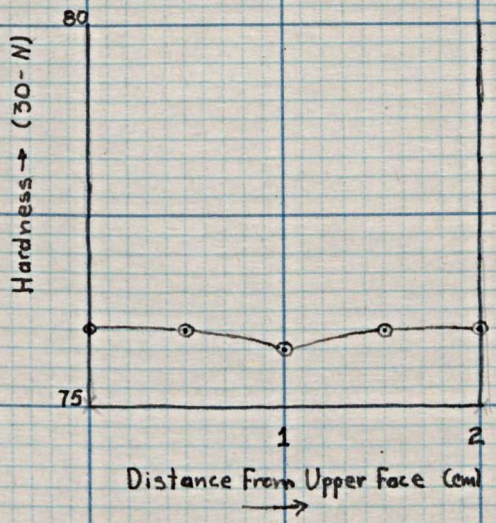


Fig 5

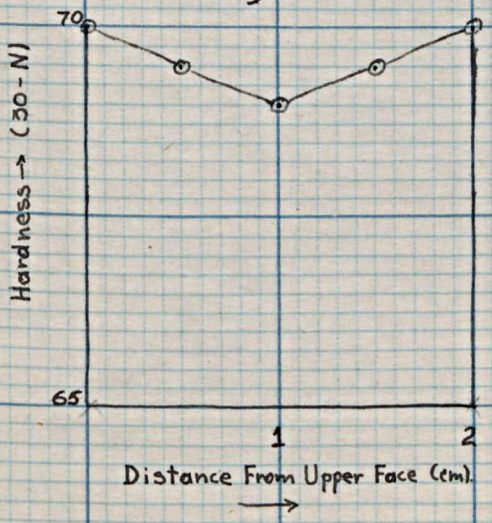
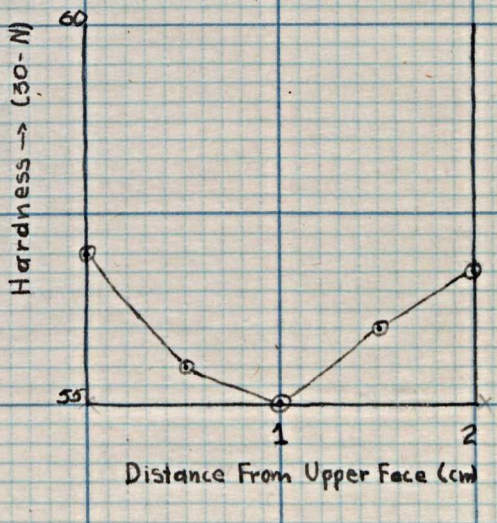


Fig. 6



DISCUSSION

Approximately 10 per cent of the boron was lost on melting. This loss was rather constant in each alloy.

In order to obtain more accurate results the castings should have been much larger. This would have enabled larger sections to be studied and the effect on the depth of hardening more accurately determined.

CONCLUSIONS

1. The optimum effect on both maximum hardness and depth of hardening was obtained by the addition of .03 per cent boron.

2. It is suspected that the boron to be effective should be in solid solution in the steel.

3. The increase in the depth of hardening increases the strength of the steel.

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